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THE PRECURSOR OF AN EXTRAORDINARILY REACTIVE HOMOGENEOUS HYDROG--ETC(U)

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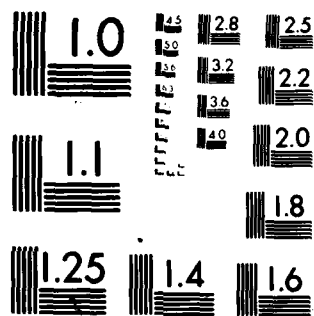
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THE PRECURSOR OF AN EXTRAORDINARILY REACTIVE HOMOGENEOUS HYDROGENATION CATALYST.

SYNTHESIS, STRUCTURE AND REACTIONS OF

[closo-1,3-η²-3,4-buten-1-yl]-3-H-3-PPh₃-3,1,2,-RhC₂B₉H₁₀]

By

M.S./Delaney, C.B./Knobler and M.F./Hawthorne

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THE PRECURSOR OF AN EXTRAORDINARILY REACTIVE HOMOGENEOUS HYDROGENATION CATALYST.

SYNTHESIS, STRUCTURE AND REACTIONS OF

[*closo*-1,3- μ -(η^2 -3,4-buten-1-yl)-3-H-3-PPh₃-3,1,2,-RhC₂B₉H₁₀]

By

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SUMMARY

The synthesis, reactions and structure of the catalyst precursor [closo-1,3- μ -(η^2 -3,4-buten-1-yl)-3-H-3-PPh₃-3,1,2,-RhC₂B₉H₁₀] (I) and the initial rates of some alkene hydrogenations catalyzed by (I) are reported.

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Sir:

In our studies of alkene reduction catalyzed by [closo-3-H-3,3-(PPh₃)₂-3,1,2-RhC₂B₉H₁₁]¹, we have noted that the rate of hydrogenation is inversely proportional to the concentration of added triphenylphosphine. This observation suggests that reversible triphenylphosphine dissociation is an important equilibrium which precedes the rate determining step of the hydrogenation sequence. The ease with which the parent catalyst could be modified through synthesis led us to explore the possibility of obtaining enhanced hydrogenation rates by replacing one of the triphenylphosphine ligands with a chelated η^2 -3,4-buten-1-yl side chain attached to one of the dicarbollide ligand carbon atoms. The resulting rhodacarborane (I), [closo-1,3- μ -(η^2 -3,4-buten-1-yl)-3-H-3-PPh₃-3,1,2-RhC₂B₉H₁₀], might well undergo irreversible hydrogenation of the alkenyl side chain under the conditions for alkene hydrogenation to produce an open coordination site on rhodium² resulting in a marked rate acceleration in the hydrogenation of alkenes. Complex (I) is among the most active homogeneous hydrogenation catalysts reported to date (vide infra), demonstrating this effect. In addition (I) is to our knowledge the first rhodium complex of the relatively rare hydrido alkene class of complexes³⁻¹¹ to be isolated and structurally characterized.

A methanol solution of [RhCl(PPh₃)₃] and a 20% molar excess of Cs⁺[7-butenyl-7,8-C₂B₉H₁₁]⁻¹² heated to reflux under nitrogen for three hours precipitated a yellow microcrystalline product in 90% yield¹³ which was recrystallized from CH₂Cl₂-ethanol under an inert atmosphere (m.p. 170-3°C dec). Elemental analysis, NMR and infrared spectra[†] supported the proposed formula for (I).

The small yellow prisms of (I) crystallized in the space group $P2_1/c$. The cell data are:¹⁴ $a = 16.494(4) \text{ \AA}$, $b = 11.193(2) \text{ \AA}$, $c = 17.006(3) \text{ \AA}$, $\beta = 122.49(1)^\circ$, $V = 2648.22(95) \text{ \AA}^3$, $\rho = 1.386 \text{ g.cm}^{-3}$ (x-ray density), $\rho = 1.229 \text{ g.cm}^{-3}$ (flotation density, aqueous KI)¹⁵. The molecular structure of I is shown in Figure I with significant bond distances and angles. The rhodium atom is symmetrically bound to the pentagonal face of the dicarbollide ligand. The vinyl moiety of the butenyl group is bound to the rhodium in such a fashion that the C=C bond is nearly parallel to the pentagonal face of the dicarbollide ligand.

A THF solution, $1.8 \times 10^{-4} \text{ M}$ in (I) and 0.13 M in trimethylvinylsilane displayed an initial rate of $2.4 \times 10^{-1} \text{ mol} \cdot \text{sec}^{-1} / \text{mol Rh}$ for the reduction of the alkene when exposed to hydrogen ($P_{H_2} = 705 \text{ mm Hg}$) at 0°C . A THF solution of $[\text{RhCl}(\text{PPh}_3)_3]$ under the same conditions exhibited an initial rate of $7.8 \times 10^{-3} \text{ mol} \cdot \text{sec}^{-1} / \text{mol Rh}$, thirty times slower than the rate exhibited by (I). A THF solution of (I) under the same conditions as described above displayed an initial rate of $8.9 \text{ mol} \cdot \text{sec}^{-1} / \text{mol Rh}$ in the reduction of 3,3-dimethylbut-1-ene. A CH_2Cl_2 solution $5.0 \times 10^{-4} \text{ M}$ in $[\text{Ir}(\text{cod})\text{P}(\text{i-Pr})_3(\text{py})]^+\text{PF}_6^-$ and 0.5 M in 3,3-dimethylbut-1-ene displayed an initial rate of $2.3 \text{ mol} \cdot \text{sec}^{-1} / \text{mol Ir}$ when exposed to hydrogen ($P_{H_2} = 600 \text{ mm Hg}$) at $0^\circ\text{C}^{5c,d}$. The compound $[\text{Ir}(\text{cod})\text{P}(\text{i-Pr})_3(\text{py})]^+\text{PF}_6^-$, apparently the most active previously reported homogeneous hydrogenation catalyst, must be used in CH_2Cl_2 due to the need for a non-coordinating polar solvent. Complex (I), on the other hand, has been found to be effective as a homogeneous hydrogenation catalyst in THF, o-dichlorobenzene, benzene and toluene.

When 1 mmol of (I) in the THF was exposed to hydrogen while in the presence 2.4 mmol of triphenylphosphine, the solution took up 1 mmol of hydrogen. Solvent removal in vacuo followed by column chromatography (silica gel, CH_2Cl_2 -hexane

eluent under nitrogen) gave an orange compound which was recrystallized from CH_2Cl_2 -heptane in 90% yield. This compound was shown to be [closo-1-butyl-3-H-3,3-(PPh_3)₂-3,1,2- $\text{RhC}_2\text{B}_9\text{H}_{10}$], (II), on the basis of elemental analysis, infrared and NMR spectra[†], thus demonstrating the facile hydrogenation of the alkenyl side chain. Complex II was identical to the product obtained from [$\text{RhCl}(\text{PPh}_3)_3$] and $\text{Cs}^+[\text{7-butyl-7,8-}\text{C}_2\text{B}_9\text{H}_{11}]^-$ ¹⁶ in methanol and was also found to be an effective hydrogenation catalyst.

When 1 mmol of (I) in the THF was exposed to hydrogen in the absence of triphenylphosphine the solution rapidly took up 1 mmol of hydrogen with the hydrogenation of the butenyl side chain and then slowly evolved 0.5 mmol of hydrogen. Use of a procedure similar to that described above for (II) gave an air sensitive dark purple compound (III) which will be reported elsewhere. At this time we suggest that (III) is a dimer similar to [$\text{PPh}_3\text{RhC}_2\text{B}_9\text{H}_{11}$]₂¹⁷.

The results reported above support the view that the great diversity of structural parameters available in metallocarborane chemistry may be usefully exploited for the development of novel catalytic systems.

[†] Satisfactory elemental analyses, infrared and NMR spectra were obtained for all reported compounds.

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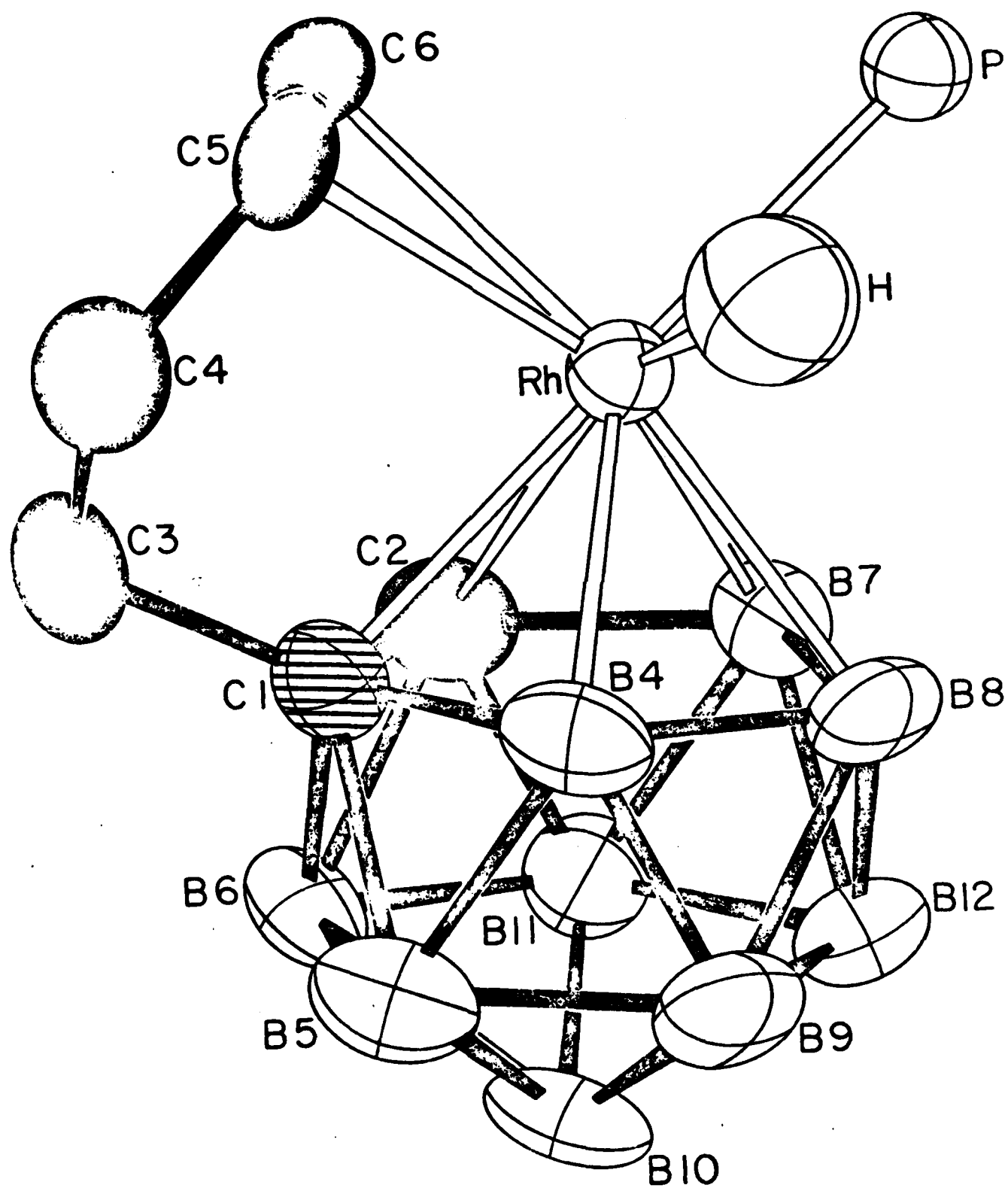
REFERENCES

1. (a) T.E. Paxson and M.F. Hawthorne, J. Am. Chem. Soc., 96 4674 (1974)
(b) G.E. Hardy, K.P. Callahan, C.E. Strouse and M.F. Hawthorne, Acta Cryst., B32 264 (1976)
2. R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 98 2134 (1976)
3. D.R. Falkowski, D.F. Hunt, C.P. Lilya and M.D. Rausch, J. Am. Chem. Soc., 89 6387 (1967).
4. T.W.S. Benfield and M.L.H. Green, J. Chem. Soc. Dalton, 1324 (1974)
5. (a) H. Felkin, G.E. Morris and R.H. Crabtree, J. Chem. Soc. Chem. Comm., 716 (1976)
(b) H. Felkin, T. Khan, G.E. Morris and R.H. Crabtree, J. Organometal Chem., 144 C15 (1978)
(c) H. Felkin, T. Fillebeen-Khan, G.E. Morris and R.H. Crabtree, J. Organometal, Chem., 168 183 (1979)
(d) R. Crabtree, Acc. Chem. Res., 12 331 (1979)
6. (a) T.V. Ashworth, E. Singleton and M. Laing, J. Organometal, Chem., 117 C113 (1976)
(b) T.V. Ashworth, M.J. Nolte and E. Singleton, J. Organometal, Chem., 117 C73 (1977)
7. G. Del Piero, G. Perego and M. Cesari, Gazz. Chim. Italiana, 105 529 (1975)
8. K.W. Muir and J.A. Ibers, J. Organometal. Chem., 18 175 (1969)
9. (a) G.R. Clark, P.W. Clark, A.J. Jones, M.A. Mazid and D.R. Russell, J. Organometal. Chem., 166 109 (1979)
(b) G.R. Clark, P.W. Clark, and K. Marsden, J. Organometal. Chem., 173 231 (1979)

10. J.W. Byrne, H.U. Blaser and J.A. Osborn, J. Am.Chem.Soc., 97 3871 (1975)
11. J. Evans, B.F.G. Johnson and J. Lewis, J. Chem.Soc. Dalton, 510 (1977)
12. The 4-(o-carboranyl)-but-1-ene may be prepared by the method of D. Grafsten, J. Bobinski, J. Dvorak, H. Smith, W. Schwartz, M.S. Cohen and M. Fein, Inorg. Chem., 2 1120 (1963) and degraded by the method of M.F. Hawthorne, D.C. Young, P.M. Garrett, D.A. Owen, S.G. Schwerin, F.N. Tebbe and P.A. Wegner, J. Amer. Chem. Soc., 90 862 (1968).
13. Yield based on rhodium consumed.
14. X-ray intensity data were collected by the θ - 2θ scan technique with MoK α radiation (graphite monochromator) on a Syntex P $\bar{1}$ automated diffractometer equipped with a scintillation counter and pulse height analyzer. Of a total of 3840 reflections examined, 2336 had $I > 3\sigma(I)$ and were used in the structure determination. The data were corrected for absorption, Lorentz and polarization effects. The structure was solved by using heavy atom methods and refined by full matrix least squares techniques, converging at $R=0.044$ and $R_w=0.048$.
15. Standard deviations are given in parentheses.
16. The n-butyl carborane may be prepared by the method of T.L. Heying, J.W. Ager, Jr., S.L. Clark, R.P. Alexander, S. Papetti, J.A. Reid and S.I. Trotz, Inorg. Chem., 2 1097 (1963) and degraded by the method in reference 12.
17. R.T. Baker, R.E. King III, C. Knobler, C.A. O'Con and M.F. Hawthorne, J. Am. Chem. Soc., 100 8266 (1978).

FIGURE 1

Molecular Structure of (I) (the phenyl rings on phosphorus and all hydrogens except the rhodium hydride have been omitted for clarity). Distances from Rh to the attached atoms are H 1.65(3), C₁ 2.211(8), C₂ 2.266(8), B₄ 2.217(9) B₇ 2.220(9), B₈ 2.217(9), C₅ 2.276(8), C₆ 2.242(8), P 2.291(2). Some significant angles are C₅-Rh-C₆ 35.2(3), C₅-Rh-H 82 (2), H-Rh-P 74(3), C₆-Rh-P 87.2 (2).¹⁵



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